Extraction and utilisation of rice bran oil. A review

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Rice bran oil (RBO) has gained wide popularity in recent years due to its considerable health benefits. RBO has found many applications in the food, pharmaceutical, cosmetics and chemical industries because of its unique properties and medicinal value. However, the lack of a widespread commercial use of RBO is largely due to its high cost when compared to other vegetable oils. RBO is obtained through the extraction of rice bran, which is a by-product of the rice milling industry. There are several techniques used to extract RBO, but solvent extraction using hexane is the most widely used conventional method for commercial extraction. The use of hexane in the conventional method has some drawbacks due to hexane's toxicity, flammability and a need for a high temperature, which, through oxidative deterioration, can result in having undesirable components in the oil that give it a rancid flavour. For these reasons, various researchers have worked to explore alternative, nonconventional techniques for the RBO extraction. This review will provide an overview of the most commonly used extraction methods for RBO as well as its existing applications in various industries.

Keywords: rice bran oil; extraction of RBO; utilisation of RBO.

INTRODUCTION

RBO has developed a considerable reputation for its numerous health benefits. It has several advantages over other edible oils because of the presence of the unique antioxidant γ (gamma)-oryzanol [1]. RBO is also a good source of other nutritionally important compounds such as tocopherols, tocotrienols and phytosterols [2, 3]. Crude RBO contains about 1.1-2.6% of γ-oryzanol, 0.2% of tocols, 70% of which is tocotrienol, and 3-5% of phytosterols and fatty acids steryl esters [2]. Rice bran is a major by-product of the rice milling process and unmilled rice is 8.0% rice bran by weight [4] (Fig. 1).

Rice bran contains 10-26% oil depending on the variety, milling process, and other agro-climatic conditions [5]. In order to extract RBO after the milling process, the rice bran needs to undergo a process called stabilisation to inactivate lipolytic enzymes and inhibit lipid oxidation. This stabilisation process is essential to prevent the deterioration of the oil and valuable bioactive compounds of the bran [6]. In order to obtain the highest yield of the oil, an economical and efficient method of stabilisation is required [7]. Many stabilisation methods have been reported, such as steaming, ohmic heating [7 - 9], ultrasound treatment [10, 11], parboiling, refrigeration, pH lowering [12] and microwave radiation [13, 14]. India is the leading producer of RBO, followed by Japan, Thailand and China. As of 2014, the global production of RBO reached 1.2 million tons, with India contributing about 75% (900,000 tons) of the total. RBO production is increasing greatly by about 50 thousand tons yearly [1]. However due to the

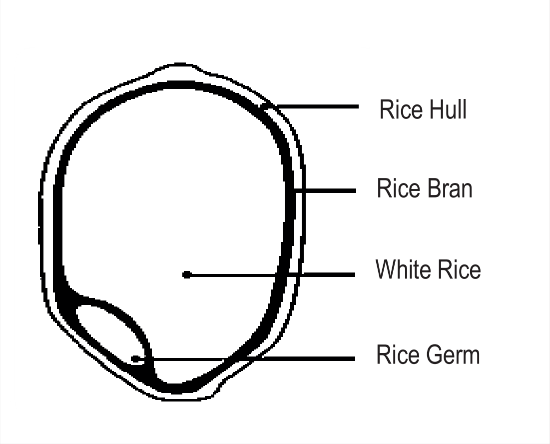

Figure 1 - Structure of Rice grain

high cost of RBO, it has not yet gained widespread commercial use [15, 16]. The development of more economical extraction methods of RBO are important for small and medium scale RBO industries [7].

EXTRACTION METHODS OF RICE BRAN OIL

RBO can be extracted either chemically (by solid-liquid extraction techniques [17, 18] or mechanically by pressing). The most commonly used techniques for the extraction of RBO are discussed in detail here.

SOLVENT EXTRACTION PROCESS

Solvent extraction is a very effective method that can generally remove very high percentages of the oil that is in any given material. Because it is so effective, solvent extraction is particularly useful for recovering oil from materials with low oil content. For example, solvent extraction is sometimes used with oil cakes that are the product of previous mechanical extraction. Subsequent solvent extraction can obtain even the small amount of oil remaining in the oil cake [19 - 22]. Hexane is the most commonly used solvent for this method, and it is both efficient and relatively inexpensive [23]. Other short chain alcohols such as ethanol and isopropanol have also been used as alternative solvents for extraction because of their greater safety [14, 15, 24].

A yield of about 92% oil was obtained from hexane extraction of ohmic heat-stabilised rice bran [8]. Oliveira et al. [21] reported various yields of 42.7-99.9% from rice bran by extraction with ethanol to rice bran ratio of 2.5:1 and 4.5:1, and temperature of 60-90°C. One study has shown that by increasing the extraction temperature from 40°C to 60°C and the solvent (hexane and isopropanol) to bran ratios (w/w) from 2:1 to 3:1, the yield of RBO also increases. Extraction at 60°C for 10 min with 3:1 solvent to bran ratio using hexane yielded about 3.6% more oil than at 40°C, while extraction with isopropanol at 60°C produced 6.4% more oil than at 40°C [15]. Extraction with liquid propane was found to yield 0.224±0.016 kg oil/kg of rice bran at 0.76 MPa and room temperature [23]. RBO extractions were also carried out with isopropanol and hexane at 40°C for 15 min. The hexane extracted almost 40% more oil than the isopropanol. By increasing the temperature up to 120°C, the yield of hexane did not increase; however, the isopropanol extracted 25% more RBO than hexane under similar conditions [24]. About 99 to 99.5% oil was reported to be extracted by solvent extraction from oleiferous seed [25]. It is worth mentioning that when solvent extraction was used to recover oil from algae, only about 0.5% to 0.7% of the oil was left unrecovered [26]. Preliminary data suggested that an optimum ratio of 5:1 solvent-meal (rice bran) can be used [14].

Generally, the crude RBO obtained through solvent extraction is further processed through chemical or physical refining in order to meet the specifications for food grade vegetable oil [14]. The solvent usually used in this method, hexane, is however flammable, volatile, toxic and it pollutes the environment [27]. Even so, the use of hexane for extraction has been considered efficient and hexane is still the most widely used solvent, despite its drawbacks [12, 17].

MECHANICAL PRESSING (COLD PRESSING)

Worldwide, mechanical pressing is traditionally the most popular oil extraction method for oilseeds [12, 17]. Mechanical pressing has been in popular use by small and medium scale oil extraction industries for commercial RBO extraction in some countries. Mechanical pressing is less expensive and less labour-intensive than using solvent extraction methods [11, 13]. The safety and simplicity of the process are advantages over the more efficient solvent extraction techniques [7]. Mechanical pressing does not involve heat or chemical treatment, thus making it an interesting alternative for conventional use because of consumer concern for natural, safe products [13]. Recently there has been an increased interest in cold-pressed oil facilities because of the better nutritional properties of cold pressed oil, compared to oil obtained from other refining process [29].

Mechanical pressing can be of two types: the screw press and the hydraulic press. The screw press is also called an expeller. It is simple, and easy to maintain and operate by semi-skilled workers [11, 30]. In comparison to a hydraulic press, the motion of a screw press is continuous and produces slightly higher oil yield than a hydraulic press [25]. The screw press method involves continuous pressing using expellers (screw press). Expellers consist of a screw rotating inside a cylindrical cage (barrel). The material to be pressed is fed between the screw and the barrel, and then propelled by the rotating screw in a direction parallel to the axis. The gradual increase in pressure helps release the oil that comes out of the press through the slots on the side of the barrel. The residual pressed cake then moves in the direction of the shaft for discharge [9, 11].

During extraction of RBO using the screw press method, only about 9 to 10% of the total oil content of the bran is extracted by pressing [9]. Mechanical extraction of oil from oleiferous seeds has recovered 80 to 85% of the seeds' total oil content [25]. It was also found that 75% of total oil can be recovered from algae [19]. Although mechanical pressing results in high quality oil, the yield is relatively low and this extraction method is generally used only for small scale extraction, specialty products or as a pre-press operation in a large-scale solvent extraction plant [9, 25]. To improve the effectiveness of this method, further modification in the equipment design is required to increase the oil recovery [9].

SOXHLET EXTRACTION

Soxhlet extraction is a common means of extracting vegetable oils. The process usually involves crushing the oil seeds and then placing them in a packed bed exposed directly to the solvent, thereby leaching the oil from the solid matrix into the liquid [31]. By using this method with heptane as a solvent at 40-60˚C, a typical yield of 15-20% RBO by weight of rice bran was obtained, while using petroleum ether as a solvent yielded 18.4% [32, 33]. Liu et al. [34] have reported a yield of about 67.73±0.37% RBO by Soxhlet extraction using hexane. About 61.2% oil was also recovered from black dates using this method with N-Hexane at 65ºC for 8 h [35]. Imsanguan et a [36] studied the efficiency of γ-oryzanol and α-tocopherol extraction from rice bran, using alternatively the Soxhlet method, supercritical CO_2 or solvent extraction. The highest yield was obtained using SC-CO_2. There were no literature references on the use of Soxhlet extraction for RBO in high quantities. The method is mainly employed for laboratory extraction purposes.

SUPERCRITICAL FLUID EXTRACTION

Supercritical fluid (SCF) is formed when a given fluid is subjected to a pressure and temperature higher than the critical point. Under these conditions, the fluid exhibits some properties of a gas and some of a liquid. SF has a density like a gas, but its diffusivity is between that of a gas and a liquid [37]. Every SCF possesses a specific critical point (Tab. I) which depends on the critical temperature and pressure of that gas/liquid [38]. Supercritical fluid extraction (SFE) is a promising technique that allows for an extract free from toxic residues, so oil extracted using SCE can be used directly without further processing [37]. The extract has an ultra-pure composition as well as other excellent features [39], and it also gives a yield comparable in terms of yield to hexane extraction method [27]. When SCF is used for extraction, there is minimal risk of solvent contamination, thermolability or unintended chemical changes that may occur during conventional solvent extraction methods [40]. Among common SCFs, carbon dioxide (CO_2) is often the most expensive supercritical solvent but it is also the one most commonly used in food industries [38]. Supercritical CO_2 (SC-CO_2) is an alternative to organic solvent extraction and has been found to be ideal for extraction of many oils. Before the CO_2 is used, it is first changed to its supercritical fluid state, i.e., beyond the supercritical point (73 atm, 31°C). The extraction process is simple when compared to the traditional method, and the SC-CO_2 is nontoxic and non-flammable [22]. A maximum RBO yield extracted by SC-CO_2 was found in the range of 19.2 to 20.4% by bran weight [41]. Balachandran et al. [27] reported a yield of 20% by weight of RBO using SC-CO_2 at 60°C, 500 bar, for 1.5 h and a CO_2 flow rate of 40 g min^{-1}, as compared to 22.5% from hexane extraction. It was observed that the oil yield can be increased by increasing the temperature to 70ºC, pressure to above 500 bar, and lengthening the extraction time. A yield of 0.222±0.013 kg oil kg^{-1} rice bran was also reported from SC-CO_2 extraction at 45ºC and pressure of 35 MPa [23]. Several researchers have investigated

Table I - Critical properties of some solvents

Solvent	Molecular weight ($gmol^{-1}$)	Critical temperature (K)	Critical pressure (atm)	Critical density (G)
Carbon dioxide	44.01	304.1	72.8	0.469
Water	18.02	647.1	217.8	0.322
Methane	16.04	190.4	45.4	0.162
Ethane	30.07	305.3	48.1	0.203
Propane	44.09	269.8	41.9	0.217
Ethylene	28.05	282.4	49.7	0.215
Propylene	42.08	364.9	45.4	0.232
Methanol	32.04	512.6	79.8	0.272
Ethanol	46.07	513.9	60.6	0.276
Acetone	58.08	508.1	46.4	0.278

Source: Reid et al., [86]

the use of SC-CO_2 for extraction of RBO [14, 22, 27, 42, 43]. However, this technology has some limitations due to the high cost of necessary equipment.

SUB-CRITICAL FLUID EXTRACTION

Sub-critical fluids are also known as hot liquid solvents or pressurised/accelerated liquid solvents [44]. They are fluids that have been compressed below their critical temperatures and still maintain their liquid state, and they are used above their boiling point by increasing the pressure. Sub-critical fluid extraction is a continuous counter-current process in which the solvent is removed after extraction by applying a vacuum at low temperature [45]. The process has the advantage of using lower temperature and pressure as opposed to the SFE method that may be expensive, due to the cost of additional pressure and temperature requirements. Various solvents including hexane can be used for sub-critical fluid extraction. Sub-critical propane and butane are also used due to their low critical temperature and pressure. They are also colourless and leave no toxic residue in the product. Yields of 89.11±0.41%, 91.42±0.31%, and 67.73±0.37% RBO, were obtained by sub-critical extraction using butane, propane and hexane, respectively. The butane and propane had better efficiency when compared to hexane [34]. In a study on oil extraction from *Nitraria tangutorum* seed using sub-critical fluid extraction (SFE) with CO_2, a yield of 12.92% oil was obtained at optimum conditions of 40 min, 0.60 MPa, 44°C and a raw material particle size of 0.45 mm [46].

Sub-critical water extraction (SWE) of RBO was also reported [47, 48]. SWE is also known as superheated water or pressurised hot water extraction [49]. The SWE process involves the use of hot water maintained in its liquid state at a temperature of between 100ºC and its critical point of 374°C under sufficient pressure of 22 MPa to maintain the liquid state. At these conditions, the water behaves like a highly hydrophobic solvent, and thus it can extract lipophilic substances from both solid and semi-solid matrixes [49, 50]. The SWE has advantages of high recovery rates and shorter extraction time when compared to SC-CO_2 [50]. Although this method gives high yield and excellent quality oil with high concentration of the health components [34], its application has yet to become popular, so data concerning SWE extraction of RBO is rather limited.

ENZYME-ASSISTED AQUEOUS EXTRACTION

Enzyme-assisted aqueous extraction of RBO has been regarded as an eco-friendly process producing a superior quality oil [51]. The use of aqueous medium for oil extraction from different oil seeds has been investigated by many researchers [26, 52, 53]. For example, this method has been studied for the extraction of corn germ oil [54], soybean oil [55], peanut oil [56], sunflower oil [57] and rice bran [26]. Although the aqueous extraction method was unsuccessful in the past because of its low oil yield, recent developments involve the use of enzymes to assist the extraction process, thus resulting in a higher yield [57]. The enzymes in this process help hydrolyse and break down the structural polysaccharides that form the cell wall, leading to release the oil into the aqueous system [6, 58].

A yield of 92.63% RBO was obtained by combining enzymatic extraction with ultrasonic treatments. Enzymatic hydrolysis was performed using enzymes (cellulose 1.2%, protease 0.6% and amylase 0.3%) at 55°C, 4.5 pH and 5.5 h hydrolysis time [10]. A maximum yield of 87.25% total oil was extracted from sunflower seed using an enzyme (viscozymes L) from Novozymes (Bagsvaerd, Denmark) and incubated at 45°C for 2 h [59]. For an enzyme-assisted extraction of wheat germ, barley germ and rice bran, different enzymes such as Protex 6L, Protex 7L, Alcalase, Fermgen, Lysomax and G-zyme 999, were tested. The combination of four enzymes gave an oil yield of 70%, while a combination of two of the enzymes i.e., 5% fermgen (protease) and 5% spezymes (cellulase) gave the highest yield of 73.1% oil. The optimum conditions were a 2:1 ratio of raw material to water, a pH of 5, hydrolysis temperature of 50°C and 5% enzyme concentration (V/W) for 20 h [28].

Enzyme-assisted extraction of RBO from full fat rice bran was reported by multiple researchers using different enzymes or mixtures of enzymes such as protease, α-amylase and cellulose [59], Neutrase and Celluclast [51], or a mixture of protease, amylase and cellulose [10]. This method is better than the traditional oil extraction process because it produces oil with better-quality attributes in terms of colour, free fatty acids, peroxide value, and phosphorus content [56].

OTHER METHODS

In literature, the extraction of RBO was also reported using methods such as; compressed liquefied petroleum gas (LPG), (due to its low cost and availability as compared to propane, n-butane and CO_2) [60], microwave assisted extraction [24] and ultrasound assisted extraction [61], which may involve passing a sound wave (example >20 KHz) to a solvent containing the raw material to increase the extraction yield [62]. The various extraction methods are presented in Table II.

UTILISATION OF RICE BRAN OIL

RBO is widely used in food, pharmaceutical and chemical industry because of its unique properties and high medicinal value [12]. The desirable health benefits and functional attribute of cold pressed of

RBO make it useful for foods, cosmetics and pharmaceutical applications [2, 7]. There is an increasing interest in the use of RBO in a wide variety of health products due to consumer's demand for natural products. It is a great source of polyunsaturated fatty acid (PUFA), and monounsaturated fatty acids (PUFA) which give it potential nutraceutical properties [63]. Recently, several nanoencapsulation and microencapsulation studies of RBO in both food and pharmaceuticals researches has been conducted to increase the stability and control the release of the bioactive compounds in RBO [64, 65]. Microencapsulated RBO has been used in preparation of *shrikhand* premix as a fat alternative [66]. In this review, the uses of the RBO are discussed in terms of food, pharmaceutical, cosmetics, food and other uses.

FOOD USES

RBO has been used extensively as a premium edible oil in many Asian counties like Japan, Korea, China, Taiwan and Thailand. In Japan, it is popularly known as 'Heart Oil' [1, 67]. It is generally considered the highest quality edible oil for cooking due to its good fatty acid profile, cooking quality and shelf life [68,

Table II - Different extraction processes for rice bran oil

S/N	Stabilization methods	Extraction methods	Oil yield	Reference
1	Hot air heating, microwave heating, roasting and steaming	Cold pressing	5.53, 4.81, 4.77 and 3.41 g 100g^{-1} rice bran for hot air, microwave, roasting and steamed stabilized rice bran	[29]
2	Sub-critical water	Sub-critical water extraction at 240°C for 10 min	249 mg oil g^{-1} rice bran	[47]
3	Not stabilized	SC-CO$_2$ at 30 and 60°C for 20 min	90 g kg^{-1} and 130 g kg^{-1} rice bran	[23]
4	Not stabilized	SC-CO$_2$ at 45°C and 35 MPa, and Propene at ambient temperature and 0.76 MPa	0.222±0.013 kg kg^{-1} rice bran and 0.261±0.005 kg kg^{-1} rice bran	[15]
5	Steaming and Ohmic heating	Extraction with n-hexane, soxhlet and enzyme-assisted	7.69%, 15.80% and 10.35% for steam heated stabilized bran and 11.78, 17.11 & 11.11% for ohmic.	[6]
6	Ultrasonic treatment	Anhydrous ethanol extraction at 80°C for 20 min	19.33%	[10]
7	Not stabilized	Soxhlet extraction with heptane for 4 h	15-20% of dry bran	[30]
8	Parboiling	Aqueous extraction (distilled water)	161 mg 100 g^{-1} parboiled bran and 131 mg 100 g^{-1} oil for raw bran	[12]
9	Ohmic heating and microwave heating	Hexane extraction	92% for ohmic and 53% microwave heated stabilized bran	[25]
10	Not stabilized	SC-CO$_2$ and compressed Liquefied petroleum gas (LPG) at 40°C/250 bar	12.68% for SC-CO$_2$ and 12.07% for LPG extraction	[60]
11	Not stabilized	Enzyme-assisted aqueous extraction and n-hexane extraction	19.07±0.26 and 22.38±0.41%	[52]
12	Parboiling	Screw press (set at five levels from 8.5 to 19.8 r min^{-1}) and distances (set between 1.0 and 1.9 cm)	8.20% oil for parboiled bran and 4.17% for raw rice bran	[11]
13	Not stabilized	Ultrasonic enzyme-assisted extraction (cellulose 1.2%, protease 0.6% and amylase 0.3%), enzymatic hydrolysis time 5.5 h, pH 4.5, temperature 55°C	92.63%	[10]

69]. RBO is stable at higher temperature and gives better taste and flavour to the foods. When used for frying, it takes less time and food absorbes 15% less oil leading a better economy [68]. It also has a very high smoke point of 254ºC, making it suitable for high temperature cooking such as deep frying and stir frying [69, 70, 71]. Nowadays, RBO is used commercially in snacks by food industries and restaurants due to its stability at high cooking temperatures and better flavour characteristics. About one-third of all Japanese restaurants in the US have shifted to RBO in the last decades [72].

Effort have been made to use RBO as an alternative shortening for bakery products. A replacement of conventional shortening with up to 50% RBO gives superior quality bread in terms of baking and organoleptic properties [68]. Numerous studies described RBO as superior cooking oil because of its nutritional and sensory properties, however, it is not widely used for commercial use due lack of awareness and economic factors [8]. It was also reported to be used as a replacement for shortening in the preparation of muffins, mayonnaise and salad dressing [68].

COSMETICS USES

RBO is growing stronger for specialty ingredients in the cosmetic or personal care market. In the cosmetics industry, it is used to produce sunscreen lotions, nail polishes, lipsticks and hair conditioners [73]. This is because of its gamma (γ)-oryzanol content acting as a protective agent against lipid peroxidation cause by UV light, and the ferulic acid and its esters in γ-oryzanol, which also stimulate hair growth and ageing [74]. A γ-oryzanol concentration of 1-2% w/w was reported to serve as natural antioxidants in protecting skin from free radicals [65]. Squalene and tocotrienols in the RBO are also important for skin softening and repair [14]. The undiluted form of RBO was reported to be a safe cosmetic ingredient [75]. In an *in vivo* assessment of nanoemulsions, developed using 10% RBO, the nanoemulsions has demonstrated a fascinating potential for use in cosmetic products due to of its improved skin moisture, low irritation potential, and maintained normal skin pH when applied to human skin [73]. An encapsulated RBO in SLN (1.28% w/w RBO) has demonstrated a higher skin hydration than a cream base, when applied for 7, 14, and 28 days. A significant improvement in skin viscoelasticity in the range of 4-5% was observed for 7, 14 and 28 days of application. However, the information regarding the application of RBO as an active ingredient for cosmetic formulation has been limited [65].

PHARMACEUTICAL USES

RBO is becoming popular in the pharmaceutical sector because of its unique properties and medicinal value [12]. The significant levels of micronutrients like oryzanol, tocotrienol, phospholipids and phytosterols in RBO make it suitable to produce nutraceutical and pharmaceutical products [32, 34, 76]. The RBO is used as a supplement for bodybuilders and athletes for muscle developments [12]. Studies have shown that the administration of RBO to both human and animals lowers the cholesterol level to an appreciable level. Likewise, the consumption of a diet containing RBO lowers the low-density lipoprotein (LDL) cholesterol by 7%. This activity was believed to be due to the phytochemicals like γ-oryzanol that is in the oil [2, 77, 78]. The tocols (tocopherols and tocotrienols) that are in the RBO possess antioxidants and anti-tumour properties [1]. It was reported that RBO can reduce the risk of bad cholesterol (LDL) by about 6-75% [74, 79] and 3-10% reported by Patel & Naik [14]. It demonstrates anti-inflammatory properties in several rodents, primate and human models. In an animals' study in which hamsters were treated with RBO, an early atherosclerosis was found to be reduced by 48% with refined RBO relative to canola and coconut oil [79].

FEED USES

The soap stock and de-oiled rice bran can be used as animal feed [80]. Unprocessed gum obtained as a by-product of degumming during the oil processing are have also found application in animal meals and pellets to increase the nutritive value [81].

OTHER USES

RBO and its by-products such as soap stock, deodoriser distillate, wet gum have currently been used for the extraction of γ-oryzanol, tocopherol and tocotrienols, phospholipids, phytosterols for nutraceutical, pharmaceutical and cosmetic applications [82-84]. A high amount of γ-oryzanol can be separated from soap stock by-product of RBO processing [71, 80]. The soap stock is also used as a source of glycerides containing mono- and diglycerides that are used as emulsifiers in food, pharmaceuticals and cosmetic industries [34, 85]. A food grade wax was also extracted from RBO [1]. The gums removed during either water or acid degumming process of RBO refining are used as surface active agents (emulsifiers) in many industries [85].

CONCLUSIONS

Rice bran is a major by-product of the rice milling process that account to about 8.0% of the total milled rice. RBO is extracted from bran through various existing methods, and many more are continuously being investigated. RBO is highly rich in phytochemicals such as gamma oryzanol, tocopherol and tocotrienol that are highly associated with health benefits.

This create a high demand for the extraction of RBO. The oil has a major application in food industries as a cooking oil, shortenings for baking, and salad oils. Pharmaceutical and cosmetics' industries are also among the largest users of the oil. There is growing interest in encapsulation technology to protect the bioactive compounds of RBO from the thermal degradation during processing and increase its stability and control release. However, the application in other industries like biodiesel has not been successful and acknowledged positively due to economic reasons.

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